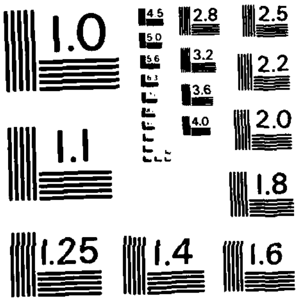
AD-A132 582 THE LOCALIZED CORROSION OF ALUMINUM ALLOYS - A REVIEW 1/1
(U) AMERICAN UNIV WASHINGTON DC DEPT OF CHEMISTRY
R T FOLEY JUL 83 TR-18 N00014-75-C-0799
UNCLASSIFIED F/G 11/6 NL

END
DATE
FILMED
9 83
DTIC


1.0
4.5
5.0
5.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 2. GOVT ACCESSION NO. AD-A132 582	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Localized Corrosion of Aluminum Alloys - A Review	5. TYPE OF REPORT & PERIOD COVERED Technical Progress Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Foley, R.T.	8. CONTRACT OR GRANT NUMBER(s) ONR N00014-75-C-0799 NR 036-106
9. PERFORMING ORGANIZATION NAME AND ADDRESS The American University 4400 Massachusetts Avenue, N.W. Washington, D.C. 20016	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Materials Division Arlington, Virginia 22217	12. REPORT DATE July 1983 13. NUMBER OF PAGES 59
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution of this document is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Localized corrosion, aluminum pitting, pit growth, morphology, oxide film

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

(Over)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

This paper was presented as a keynote address at a conference on the Control and Exploitation of the Corrosion of Aluminum Alloys held at Cranfield, Bedfordshire, England, on April 5-8, 1983.

The review was organized by a consideration of the four steps involved in localized corrosion.

1. Adsorption of the reactive anion on the oxide covered aluminum.
2. Chemical reaction of the adsorbed anion with the aluminum ion in the aluminum oxide lattice on the precipitated aluminum hydroxide.
3. Thinning of the oxide film by dissolution.
4. The direct attack of the exposed metal by the anion, perhaps, assisted by an anodic potential.

The experimental work reported in the literature is evaluated within this framework.
(204 references)

Accession For
NTIS GRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification

By
Distribution/
Availability Codes

Dist	Avail and/or Special
A	

THE LOCALIZED CORROSION OF ALUMINUM ALLOYS - A REVIEW

R. T. Foley
Chemistry Department
The American University
Washington, D. C. 20016

I. INTRODUCTION

Localized corrosion, which usually appears as pitting, crevice corrosion, or certain aspects of stress corrosion cracking, is a multi-step process. Once this is recognized the large number of apparently unrelated investigations assume a certain coherency - the experimental findings fit into the pattern which is developed from the assembly of the individual steps. The divergence of opinion among investigators comes when the attempt is made to magnify the importance of a single step to the whole, implying that the significance of this individual step overshadows all other steps. For example, the first step in a surface process, such as pitting, must be the adsorption of some reactive species. Being the first step, its importance is obvious. However, to propose that pitting can be explained in terms of an adsorption theory is not only presumptuous, but misleading, because it implies that the following steps are of relatively minor importance. Like the individual links in a chain, all steps are important and if any of the steps (or links) are eliminated the process will not go forward.

What is intended to do in this review is to first, briefly summarize the experimental observations that have been reported in the literature during the past 70 years. An inspection of the literature reveals that there is a general acceptance regarding the involvement of certain physical or chemical processes in the localized corrosion of aluminum alloys. There is not general agreement with respect to the relative importance of each of these processes. But, it is possible to write down the individual steps in the multi-step process as dictated by the experimental findings reported in the literature. Then, the investigations conducted during the last 10 years are reviewed within the context of the proposed multi-step process of localized corrosion.

Over the last 70 years a tremendous number of investigations, both in the field and in laboratories, have been conducted on the corrosion of aluminum. A bibliographic survey of the chemical aspects of the corrosion of aluminum up to 1980 lists about 1000 papers. This survey does not include reports of stress corrosion cracking, fatigue, or metallurgically oriented studies, all of which would be required to adequately describe the corrosion of aluminum. In the following, the references that will be cited will be typical rather than comprehensive. The purpose will be to draw from these reports certain well-founded, and well-accepted conclusions useful in identifying the individual steps in the multi-step process of localized corrosion.

It was recognized as early as 1912 that aluminum was corroded by salt solutions (1) and further, that this corrosion was enhanced by impurities. Subsequent investigations over the years (2-24) elaborated on this behavior and the general impression was developed that the chloride ion was unique in promoting the corrosion of aluminum. In recent years this uniqueness has been discounted, and the work unique has been replaced by the term specific. It was observed in 1916 that aluminum was corroded by organic acids such as acetic acid (25). This was not a pitting type of attack but the information gathered by such studies was useful in formulating a mechanism for localized attack. Subsequent investigations of the corrosion of aluminum alloys by organic compounds (26-32) were numerous and can be related to localized corrosion through the relative tendencies of anions to form soluble complexes (33-42). The notable case illustrating complex formation was the enhanced corrosion of aluminum in fluoride ion solutions (43-48) in which the existence of aluminum fluoride complexes was well recognized.

Whereas, it was very evident from the start that the most serious cases of aluminum corrosion involved anions, such as the halides, it was also apparent that aluminum would corrode in pure water or water relatively free of electrolytes (49-56). Moreover, it was observed that certain inorganic ions and organic molecules were effective in inhibiting corrosion (57-77). The observation that aluminum was passivated in chromate solution was made as early as 1924 (57).

The essential role of the oxide film on aluminum was mentioned in 1920 (58) and subsequent reports (59-89) emphasized this unusual feature of aluminum behavior. It was recognized that the oxide film could be produced by anodizing (90-94) as well as by exposure to air. This encouraged studies of the structure of the film as well as the corroding metal (95-110) and attempts were made to correlate structure with corrosion rates. The colloidal nature of the aluminum hydroxide reaction product and the relationship between this colloidal character and aluminum corrosion was recognized many years ago by Latvian workers (111-115). The colloidal nature of aluminum hydroxide and the oxide film on aluminum is of tremendous importance in the initiation of aluminum pitting and subsequent propogation. It suggests that the whole problem can be better approached by employing the principles of colloid chemistry rather than solid state physics. Unfortunately, this Latvian work has been unrecognized or simply ignored by most corrosion scientists. The chemical reactions of aluminum are, in one sense, unusual in that aluminum is amphoteric, soluble in acid solutions as well as alkali (116-120). This fact bears heavily in the formulation of localized corrosion mechanisims.

A complicating factor in aluminum corrosion is the composition of the alloy (121-127) but this is a consideration that aluminum shares with most other metals. It does appear that galvanic attack (128-134) on aluminum is greater than with other metals due to its activity.

A number of strictly electrochemical studies (135-147) have been made, recognizing the important role of changes in the electrode potential during the corrosion reaction. These studies have included polarization curves and the measurement of pitting potentials which are discussed in more detail below.

In the literature over the last several decades a number of related factors have also been examined. These include the temperature effect of aluminum corrosion in aqueous systems, corrosion by gases such as CO_2 and SO_2 in water, and the initiation of corrosion by photochemical energy. These topics are not covered in this review. Stress corrosion cracking is only considered in connection with some work wherein the solution in the advancing crack of a stress-corroding specimen was analyzed.

II. STEPS INVOLVED IN LOCALIZED CORROSION

It is generally accepted that the following four steps are involved in localized corrosion. These steps are listed in their time sequential order, if not their order of importance.

1. Adsorption of the reactive anion on the oxide covered aluminum. (It is assumed here that the transport of the reactive species from the bulk solution to the metal surface is occurring at sufficient rate).
2. Chemical reaction of the adsorbed anion with the aluminum ion in the aluminum oxide lattice

or the precipitated aluminum hydroxide (this may be an exchange reaction).

3. Thinning of the oxide film by dissolution. (This step includes, also, the process which has been described as "penetration" of the oxide film by the aggressive anion).
4. The direct attack of the exposed metal by the anion, perhaps, assisted by an anodic potential. This is sometimes called "pitting propagation"

III. THE ADSORPTION STEP

The adsorption of anions on the oxide-covered aluminum surface which would promote pitting corrosion has been viewed as, a competitive process. That is, chloride or another aggressive ion is adsorbed competitively with hydroxyl ions or water molecules which would, if adsorbed, tend to promote passivity.

There is substantial experimental evidence for the adsorption of anions and particularly for the adsorption of chloride as a preliminary step to pitting. Videm (56) measured the pick-up of chlorine-36 on oxide covered aluminum surfaces by autoradiography before film breakdown and during the pitting corrosion process. No pickup was detected before breakdown supporting the idea that the initial adsorbed Cl^- formed a soluble complex that diffused out into the solution. During pitting corrosion there was a heavy pickup in the pits with restricted diffusion. The conclusion from Videm's work is that chloride is adsorbed, and the main adsorption occurs at sites which will subsequently be pits. Berzins et al (148) measured adsorption isotherms on corroding Al with $^{36}Cl^-$ with similar results. The chloride adsorption was mainly localized to the corroding pit sites.

Other investigations with radioactive chromium (149) and radioactive sulfur (150) confirmed the adsorption of chromate while inhibiting corrosion in NaCl solution and the adsorption of dibutyl sulfide in H_2SO_4 solution.

With the employment of more sophisticated analytical tools, the adsorption of, not only chloride ion, but other inorganic ions on oxide covered aluminum when immersed in aqueous electrolytes has been definitely established. Using secondary ion mass spectroscopy, Wood, et al (151) detected substantial adsorbed Cl^- at the oxide-solution interface but none in the bulk oxide. The sample used was 99.99% Al covered with a 720 Å barrier type oxide film immersed under open circuit conditions for 6 hours in a KCl solution. That is, it was not necessary to use an applied potential to achieve substantial adsorption. Experiments with chromate produced similar results. Immersion of the aluminum in 1M potassium chromate-dichromate solution at pH 7.3, again gave a high concentration of adsorbed chromium at the outer oxide-solution interface.

Augustynski (152) used X-ray photoelectron spectroscopy (XPS) to measure the adsorption of Cl^-, $SO_4^=$, ClO_4^-, NO_3^-, $CrO_4^=$, and molybdate on Al of 99.99% purity. All of these anions were adsorbed. With respect to Cl^- the photoelectron spectra showed a strong Cl 2p signal. The binding energy was close to that of $AlCl_3$ but the Author did not draw a definite conclusion with respect to the form in which the chlorine resided on the surface. The adsorption was potential dependent. The relative concentration of Cl^- in the oxide film increased from 3 atomic percent at the open circuit potential to 12-13 atomic percent near the critical pitting potential. In common with other studies the chloride was found to be located in the outer 15-20 Å of the film.

The adsorption of ions on a barrier type oxide film produced in borate solution was also studied with x-ray photo-electron spectroscopy by Konno et. al. (198). After immersion of the oxide film in distilled water for 3 days it was observed that the OH^- concentration in the outer part of the film increased by a factor of 3. When immersed in chromate and phosphate solution it was observed that CrO_4^{2-} and PO^{3-} ions were adsorbed on the oxide surface to form a mono- or bi-layer. This reaction layer hindered the hydration reaction. From this study it would be concluded that in the absence of compound-forming species (chromate) the oxide would be hydrated and pass into the colloidal state.

From these studies we conclude that not only chloride, or the so-called "aggressive" anions adsorb, but anions such as sulfate and chromate as well. This, then, shifts the question to the nature of the compound formed upon adsorption.

The adsorption of anions on oxide-coated aluminum has been adequately demonstrated. Further, it may be deduced that this adsorption should be non-uniform. The surface examination of metals gives positive evidence with respect to the heterogenity of the metal surface even in the case of very pure metals. A modern view of the metal surface will disclose terraces, kink sites, and various types of dislocations. A thin oxide layer would tend to replicate this geometry. It is further known from studies such as those employing the field ionization microscope that the rate and extent of adsorption and, indeed, chemical reaction, varies with crystal orientation. The activity of a catalytic surface depends on the number and type of "active centers". It is then reasonable to expect enhanced adsorption and surface activity at imperfections or flaws in the oxide film. The case for the role of flaws in the oxide film functioning as "active centers" has been convincely made by Richardson and Wood (153-4). It should then be concluded that the site of anion adsorption should be at flaws or dislocations in the oxide film.

Experimentally it has been demonstrated that rapid adsorption of anions takes place at open circuit potential, that is, an applied potential is not required for extensive adsorption. Considering the electrical properties of aluminum oxide, this is understandable. The isoelectric point for aluminum oxide is about 8.9-9.2 (155). The isoelectric point for oxide covered aluminum according to Campanella, et al (156) is about the same although the measurements are not very precise. The isoelectric point does not seem to vary appreciably with chloride concentration (155). It would be expected then that in solutions of pH between 4-10 the aluminum oxide particle would be positively charged, attracting negative ions. The zero charge potential of oxide-covered aluminum measured in 0.01M KCl is -0.523 V (NHE) (157). The critical pitting potential of Al has been reported by Nisancioglu and Holtan (158) as -0.52 V (NHE) in 3% NaCl solution at 30°C. The correspondence of these values suggests the possibility that the influence of potential, as expressed by the critical pitting potential, is to move the potential of the aluminum surface above the point of zero charge. This would lead to enhanced adsorption because specific adsorption of chloride ions would be expected to occur below the point of zero charge.

Any discussion of the initiation of pitting regardless of the proposed nature of the first process should include a consideration of the significance of the pitting potential. As mentioned above, very early in research in corrosion science the effect of the electrical potential on the corrosion of aluminum was investigated in many laboratories. With regard to the localized corrosion of aluminum the potential enters into the mechanism in two ways, first in connection with pit initiation and secondly, with pit propagation. It has been postulated that the potential enters into the initiation step by providing the potential for anion adsorption on the surface.

Most work has been done with chloride solutions and reliable values for the critical pitting potential have been documented as reported below. But, once the pitting process has been initiated, metal dissolution can occur at lower potentials - cases have been reported for much lower.

The measurement of the critical pitting potential of aluminum and its significance has been the subject of considerable study at Trondheim (147, 158-161). Initially, Broli and Holtan (159) examined three different methods for the determination of the pitting potential and the protection potential of aluminum in dearated solutions of 3% NaCl. These methods were, 1) a potentiodynamic method with continual change of potential at scanning rates of 1 to 100 mV/min; 2) a quasi-stationary method using a stepwise change of potential, eg., lmV/min to 10 mV/min., the entire experiment taking 6-8 hours; and 3) a stationary method which involved a stepwise change of potential in which the potential was kept constant until a constant current was established, the experiment taking 4-6 days. With regard to the first method it was found that the pitting potential, E_p, depended on the scan rate. Further, the E_p values with the three methods varied over the range of -517 mv (SCE) to -713 mv (SCE), the latter being obtained by the stationary method and the only value representing electrochemical equilibrium. The protection potential, E_{pp}, also varied with the method and only for the stationary method coincided with E_p. Broli, et al (160) continued the investigation by measuring the effect of potential and chloride concentration on the pitting potential. The potential dependence for the incubation time, τ, i.e. the time required for appreciable anodic current to flow at a given anodic potential could be expressed by

$$\frac{1}{\tau} = k' \quad (E - E_p), \qquad [1]$$

E being the applied potential, and k', a reaction rate constant. k' is a function of Cl^- ion concentration

$$k' = a\, c_{Cl^-}^{b} \qquad [2]$$

in which b is the slope d log k'/d log c_{Cl^-}.

The pitting potential was found to decrease with increasing Cl^- ion concentration but not linearly. The rate of initiation, $1/\tau$, was found to increase with Cl^- ion concentration.

The results of these investigations were summarized by Nisancioglu and Holtan (158). Whereas both current-controlled methods and potential-controlled methods have been used in the measurement of the critical pitting potential the most reliable is the potentiostatic method - a stationary method. A comparison of the values is complied in Table I for a 99.53% Al alloy (0.25 Fe, 0.18 Si) (158). The methods give values in close agreement. When critical pitting potential measurements made over a period of some years were reviewed the following conclusions were drawn:

(a) Pits almost never initiate at $E < -0.76$ V (SCE)

(b) Pits seldom initiate at $E = -0.76$ V (SCE)

(c) Pits often initiate at $E = -0.75$ V (SCE)

(d) Pits always initiate at $E > -0.75$ V (SCE)

Attempts have been made to use the pitting potential as a criterion for the susceptibility of different aluminum alloys for pitting. These attempts have been unsuccessful, understandingly, because the adsorption step is not dependent directly on the alloy

Table I. Re-analysis of the data of Broli for the critical pitting potential of Al alloys in 3% NaCl obtained by various methods of measurement. Quasi-stationary results were obtained by stepwise scanning. Values with asterisks have been obtained in the present work. Potentials are in mV(SCE). (from ref. 158)

Alloy	Temp. (C)	Gas bubbled	Quasistionary potentiokinetic		Stationary potentiokinetic	Potentiostatic	Galvanodynamic (10 A/min)	Quasi stationary galvanokinetic (10 A/min)	Galvano static	Open circuit
			(1mV/min)	(10mV/min)						
1 S-½ H*	0	N_2	-750	-720	-740	-730	-680	-710		
		O_2	-740	-720	-750	-750	-680	-700		
	30	N_2	-750	-750	-780	-780	-770	-730	-750	-760
		O_2	-760	-750	-770	-770	-720	-720		
	0	N_2	-750	-720	-750	-740				

* Al = 99.53, Si = 0.18, Fe = 0.25

composition. This point was established by Nilsen and Bardal (161) who measured the pitting potential, E_p, the protection potential, E_{pp} and, $E_{crit.}$, above which the sample pitted and below which it did not, for four aluminum alloys. Two methods were used, a potentiodynamic method and a potentiostatic method. The results are given in Table II. The significant finding was that E_p and E_{pp} for the four alloys were within 25 mv, concluding that the pitting potential was not determined by the composition of the aluminum alloy (within the range studied).

Similar conclusions were arrived at by Nisancioglu and Holtan (158) who used alloys of composition a) 4.09% Mg, 0.54% Mn, 0.25% Fe, 94.91% Al, and b) 4.20% Mg, 0.56% Mn, 0.25% Fe, 94.76% Al. The values for the critical pitting potential as determined by the potentiostatic method fell in the range of -740 mV (SCE) to -770 mV (SCE), as did the values for the 99.53% Al alloy.

Generally speaking it can be said that the critical pitting potential is a reproducible expermental measurement characteristic of pitting initiation. It refers to the electrical potential difference between the oxide film and the electrolyte. On the other hand the protection potential refers to the electrical potential that exists between the electrolyte and those phases that are present after pitting initiation occurs. When a stationary method is used for measurement they coincide, i.e., electrochemical equilibrium has been established.

Table II Determined Characteristical Potentials (from ref. 161)

	Potentiodynamic method			Potentiostatic method
Alloy	E_p	E_{pp}	E_p — E_{pp}	E_{init}
99Al	-730	-750	20	$-740 < E_{init} < -730$
Al-2.7Mg	-740	-765	25	$-755 < E_{init} < -745$
Al-4.5Mg-Mn	-740	-775	35	$-760 < E_{init} < -750$
Al-1Si-Mg	-720	-760	40	$-745 < E_{init} < -735$

IV. THE CHEMICAL REACTION STEP

At this point the question relates to the type of species formed by the adsorbed anions with the oxide coated aluminum surface. There is substantial experimental evidence that stoichiometric compounds are formed at this stage by chemical reaction, as contrasted with loosely held chemisorbed species.

The Engell-Stolica method (162) has been very useful in establishing the nature of the species involved at this stage. In the Engell-Stolica method the aluminum electrode is potentiostated in the passive range, a known concentration of an aggressive anion is injected into the solution, and the "induction time" for pitting is measured (Figure 1). This induction time is the time required for a sharp rise in the anodic current to occur. A relationship between the induction time and the concentration of aggressive anion allows an estimation of n, the number of anions associated with a single surface site during the primary pitting process (23,163).

The reasoning proceeds as follows. The reciprocal of the induction time, $1/\tau$, is taken as the rate of pit initiation, i.e., the number of events per unit time. The rate equation is then

$$\left(\frac{1}{\tau}\right) = k\,[Al^{+++}]^{m}\,[X^{-}]^{n} \qquad [3]$$

wherein k is the rate constant, $[Al^{+++}]$ is the aluminum ion concentration, and m and n are the respective orders of reaction. The logarithm form of [3] is

$$\log\left(\frac{1}{\tau}\right) = \log k + m \log [Al^{+++}] + n \log [x^{-}] \qquad [4]$$

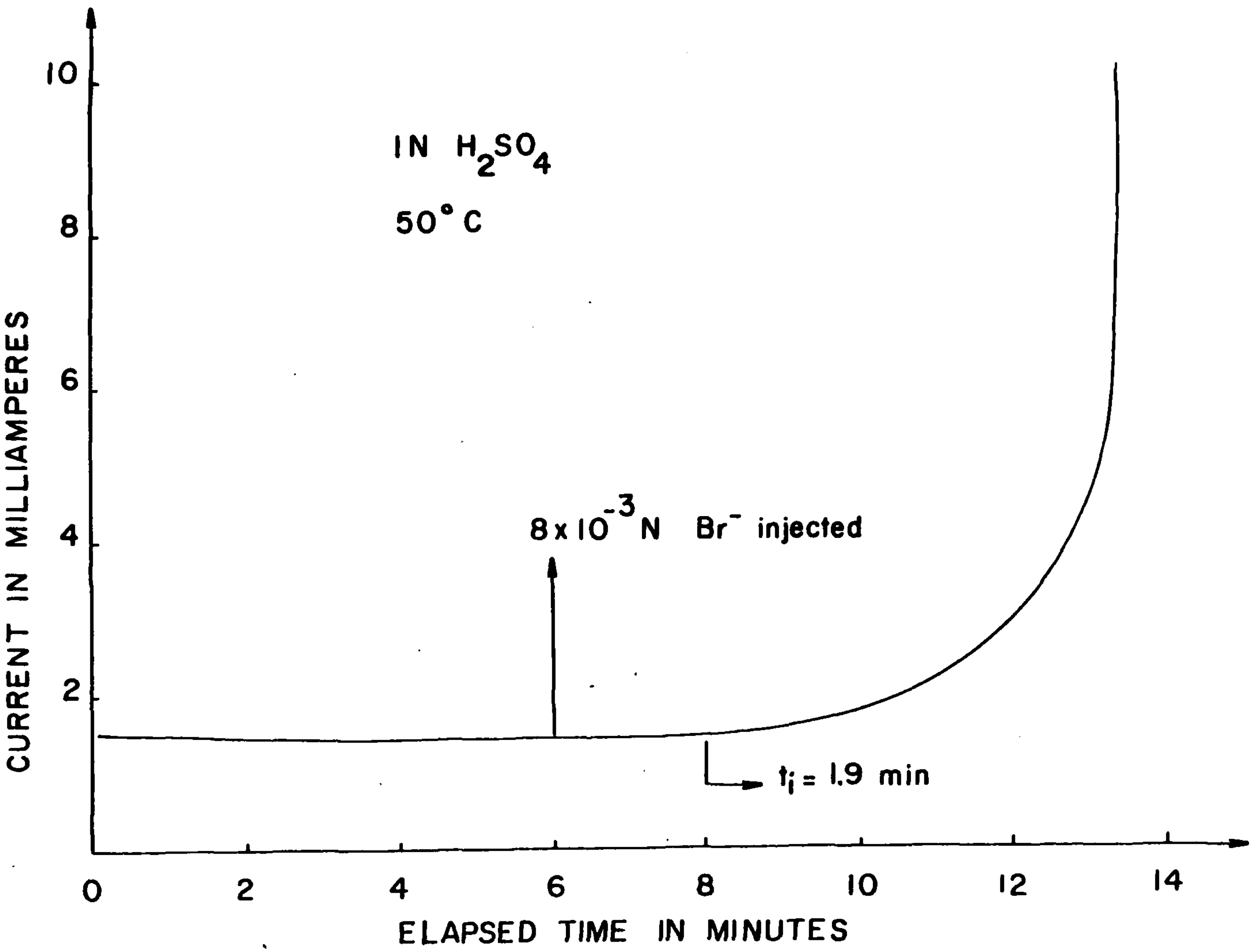


Fig. 1 A typical pitting initiation and propagation curve

Thus, if k and $[Al^{+++}]$ are taken as constant, then the plot of log $(1/\tau)$ vs. log $[X^-]$ will give n, the order of reaction with respect to X^- ions. We now have reason to think that the term m log $[Al^{+++}]$ is only constant for a specific halide reaction and that m is equivalent to the number of lattice ions involved in a surface reaction site, i.e., the coordination number of the surface in the sense used by Laidler and others in their development of the theory of absolute rate of surface reactions (164). At constant halide concentration, $(1/\tau)$ will be proportional to the rate constant and

$$\left(\frac{1}{\tau} \right) = Ae^{-Ea/RT} \qquad [5]$$

Thus a conventional Arrhenius plot of log $(1/\tau)$ vs. the reciprocal of the temperature will yield the apparent activation energy for the initiation process.

Some results for the stoichiometric number for the pitting of aluminum and two aluminum alloys in chloride and bromide solution are given in Table III. These results suggest that at low pH, about one, species such as $AlBr_4^-$ are formed, at neutral pH's, $AlBr^{++}$, and at intermediate pH's, complexes with n = 2 to 3. The energies of activation for the pitting reactions in bromide and chloride solutions are in the range indicative of a chemical reaction. They are higher in acid solution, pH = 3, than at

Table III Stoichiometric number, n, for pitting of aluminum alloys by Cl- and Br- (from ref. 171)

Alloy	Aggressive anion	pH	Order of reaction, n
Al 1199	Cl-	0.00	n = 4
Al 7075	Cl-	0.3	n = 4-8
Al 7075	Br-	0.3	n = 4
Al 1199	Cl-	3.56	n = 1.5
Al 1199	Br-	3.56	n = 2.5
Al 7075	Br-	5.8	n = 2
Al (99.995%)	Cl-	6.0	n = 2
Al 7075	Cl-	5.8	n = 2
Al 1199	Cl-	5.9-6.1	n = ~1
Al (99.53%)	Cl-	neutral	n = ~1

pH 0.00 and 0.3 obtained with 1N H_2SO_4; pH 3.56 with a saturated solution of potassium acid tartrate; pH 5.8 with 1N Na_2SO_4; pH 5.9-6.1 with 0.1-3M KCl.

pH = 5.8, in agreement with the order of reaction (Table IV). The "induction time", τ, in the Engell-Stolica method should be interpreted in a statistical sense. It measures an average rate of reaction over the whole surface to produce a measurable rise in current. It is not a measure of formation of the first single pit. In fact, recent examinations with the scanning electron microscope give evidence that during the "induction time" micropits have already formed.

From the XPS investigation of Augustynski (152) it was concluded that once certain anions were adsorbed, they reacted chemically. Thus, chromate was observed to adsorb on oxide covered aluminum. In the film produced in Na_2CrO_4 solution the adsorbed chromium was present as CrO_3 and $CrO_4^=$ ions so the film was then a mixture of hydrated chromium III and aluminum III oxides as well as chromium VI species. In the same investigation the results obtained by adsorption from nitrate solution support the idea that NO_3^- is reduced to NH_4^+. Further, results obtained with nitrate-chloride solutions again offer evidence of the competitive nature of adsorption in that the presence of nitrate retards the adsorption of chloride.

A number of investigators have concluded from their work on pitting in chloride solutions that intermediate soluble complexes are formed. Foroulis and Thubrikar (165), using the Engell-Stolica method to measure pit initiation on pure Al in

Table IV Activation energies for pitting initiation reaction of aluminum alloy Type 7075 with halides (from ref. 163)

	E_a (kcal $mole^{-1}$)	
Anion	pH 0.3	pH 5.8
F^-	—	4.6
Cl^-	18	12
Br^-	26	10
I^-	6.6	—

neutral solutions, proposed the formation of a soluble, basic chloride salt, $Al(OH)_2Cl$. Stirrup, et al (166) in their study of pit formation in chloride solutions found a logarithmic dependence of the critical pitting potential on chloride concentration. They concluded that the Cl^- ion reacted directly with the surface to promote pitting and further, that the reason that chloride was aggressive was due to the solubility of the aluminum-chlorine compound. Hagyard and Santhiopillai (39) developed a pitting mechanism based on the specific ability of $AlCl_3$ solutions to activate passive aluminum. Further, compounds such as $Al(OH)_2Cl$ and $Al(OH)Cl_2$ have been characterized by Turner and Ross (167) in their study of the hydrolysis of aluminum chloride. The work of Sussek, et al (168) in their study of pit formation on oxide free pure aluminum in chloride and sulfate solutions supports the concept that a primary step is the formation of transitory complexes such as

$$Al^{\circ} + 2Cl^- = AlCl_2 \text{ (adsorbed)} + 2e \qquad [6]$$

$$AlCl_2 \text{ (adsorbed)} = AlCl_2^+ + e \qquad [7]$$

In summary of the chemical reaction step, it can be said that there is substantial evidence for the formation of well-characterized aluminum-anion reaction products. The first of these are aluminum complex ions such as $AlCl^{++}$, $AlCl_4^-$, $Al(OH)Cl_2$, and $Al(OH)_2Cl$ which may be transitory. The second are stable, covalent, compounds such as those formed with $SO_4^=$, such as the basic aluminum sulfate (169)

$[Al_2(OH)_2\ (H_2O)_8]\ (SO_4)_2 \cdot 2H_2O$ and the hydrated chromium oxides mentioned above.

The chemical reaction between aluminum and the chloride ion has been represented (170) by a potential energy surface as shown in Figure 2. Starting on the right the low energy compounds, Al_2O_3 and $Al(OH)_3$ react with Cl^- ion to go through stages represented by $Al(OH)_2Cl$ and $Al(OH)Cl_2$, and then through transitory complexes such as $AlCl^{++}$ and $Al(OH)^{++}$.

V. THINNING OF THE OXIDE

Aluminum is a very reactive metal and owes its stability in normal atmospheres to a protective oxide. In the earliest investigations concerned with the pitting of aluminum in chloride solution the chloride ion was characterized by its ability to "penetrate" the oxide film. If, by "penetration" is meant the diffusion of the chloride ion through the aluminum oxide lattice it can be safely said that this mechanism has been thoroughly discounted during the last few decades. On the other hand if what is meant is the formation of soluble compounds or transitory species at critical sites then the concept can be justified by extensive experimental evidence.

The protective oxide on aluminum has been traditionally regarded as inert. That is, although the film may include cracks or fissures, it did not dissolve in aqueous solutions. Such is

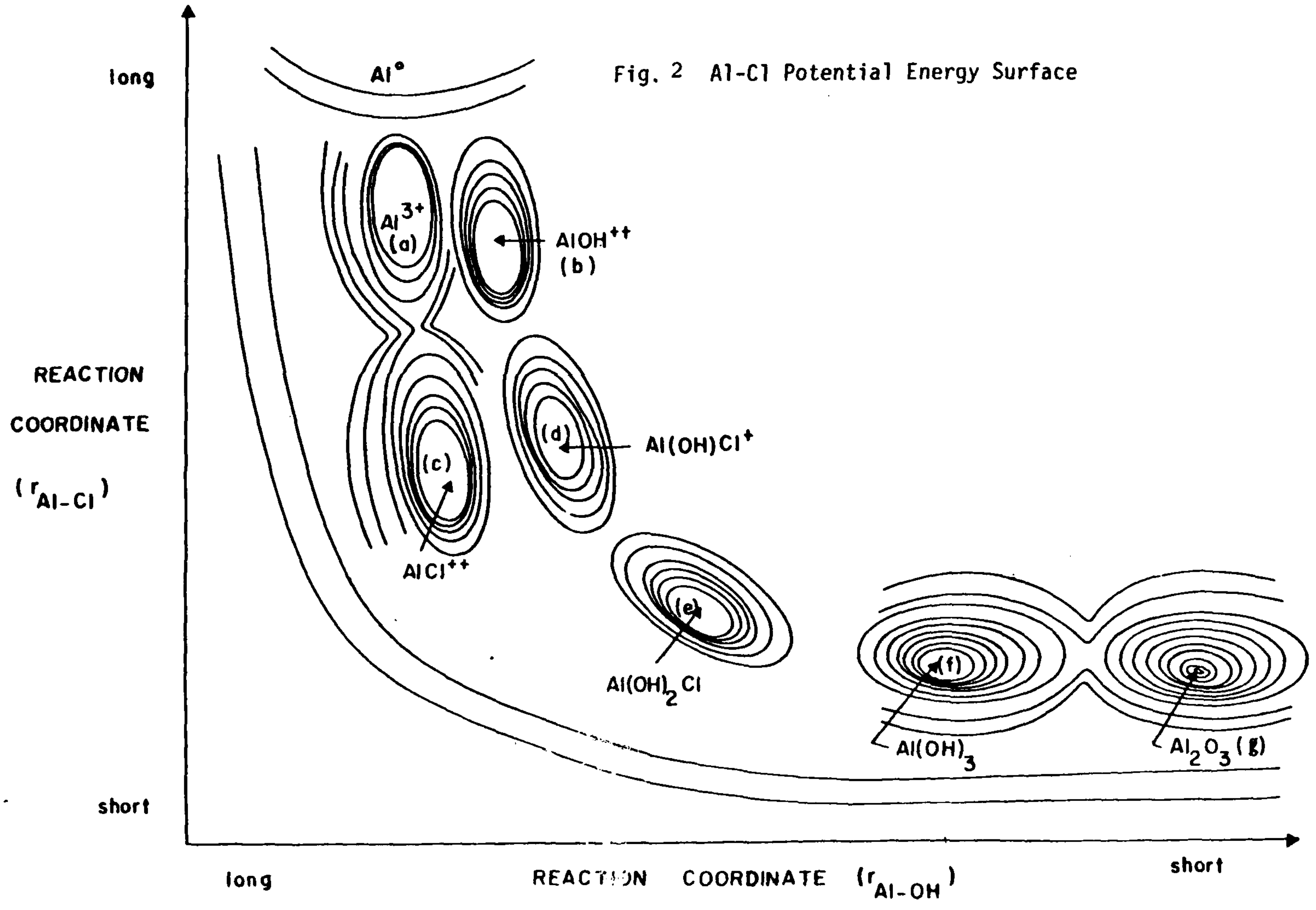

long
REACTION
COORDINATE
(r_{Al-Cl})
short
Al°
Al^{3+}
(a)
$AlOH^{++}$
(b)
(c)
$AlCl^{++}$
(d)
$Al(OH)Cl^{+}$
(e)
$Al(OH)_2Cl$
(f)
$Al(OH)_3$
Al_2O_3 (g)
long
REACTION COORDINATE (r_{Al-OH})
short

Fig. 2 Al-Cl Potential Energy Surface

not an accurate view of the oxide film. Considering alumina, ($\alpha - Al_2O_3$), which would be expected to be more stable than the oxide film on aluminum metal, the solubility in various concentrations of NaCl is reported in Table V. With regard to this analysis it should be mentioned that aluminum exists in solution (172) as (a) monomeric species, as Al^{+++}, $Al(OH)^{++}$, $Al(OH)_2^{+}$, and $Al(OH)_4^{-}$; as (b) polynuclear species containing 20-100 Al atoms; and as (c) large, solid $Al(OH)_3$ particles; all depending, of course, on the pH of the solution. The analysis given in Table V was done spectrophotometrically with Eriochrome Cyanine R reagent (173) and only measured the monomeric species. It did not measure the concentration of polymers with a basic unit structure of $Al(OH)_2Cl$ which would be expected to form in light of the above discussion. But, these experiments did demonstrate that alumina is indeed soluble in aqueous solutions.

These results follow those previously reported by Lorking and Mayne (16,47). They measured the solubility of anhydrous aluminum oxide specimens produced by anodizing aluminum at room temperature in 3% tartaric acid producing a "non-porous" type of oxide. They found that the oxide film so produced was sufficiently soluble in 24 hours in solutions of chloride, sulfate, benzoate, phosphate, citrate, and chromate to give detectable quantities of aluminum in solution. The rate of corrosion of aluminum, except for chloride solution was related to the initial

Table V Amount of aluminum ions dissolved in 100 ml of different NaCl concentration solutions (from ref. 177)

Concentration of NaCl	Aluminum powder (10g)	Alumina (10g)
1.00N	41 ± 2 μg	231 ± 14 μg
0.75N	54 ± 3 μg	258 ± 15 μg
0.50N	65 ± 4 μg	322 ± 19 μg
0.35N	54 ± 3 μg	358 ± 21 μg
0.25N	54 ± 3 μg	433 ± 28 μg
0.10N	67 ± 4 μg	476 ± 28 μg

rate of the solution. In the solutions other than chloride the initial anodic reaction was considered to be the repair of the anhydrous oxide film. In chloride solution, instead of aluminum oxide being formed, according to these investigators, soluble aluminum chloride was formed. A comparison of the rate of solubility of aluminum oxide in 0.1 sodium chloride and 0.1 N-sodium fluoride (47) explains the much higher rate in fluoride solutions in the pH range of 4-8, the solubility is explained by the fact that aluminum forms a series of complexes ranging from AlF^{++} to $AlF_6^{\equiv}$.

These studies offer independent evidence for the proposition that even in the absence of other effects, mechanical, etc. the oxide film on aluminum would be expected to be thinned upon exposure to aqueous solution.

The traditional view of the oxide film on aluminum participating in a corrosion reaction in aqueous solution has been one of an essentially anhydrous inert barrier. A more realistic view of the nature of the film participating in a corrosion reaction occurring over an extended period of time must involve a recognition of the colloidal state of the oxide. This view of the corrosion reaction has been well presented by Liepina et al in a series of papers (111-115). The corrosion reaction is viewed in terms of colloidal-chemical effects occurring on metal surfaces. The following sequence for the aluminum reaction was proposed for the reaction in KCl solution,

Al → $AlCl_3$ → polyoxychloride intermediates →
amorphous gels → bŏehmite → bayerite → hydrargillite.

If the aluminum oxide does exist in collidal form it would be expected that chloride ion will peptize it and render it dispersable. This whole approach to corrosion reactions in aqueous solution has received inadequate attention.

If the oxide film on the aluminum surface were completely uniform physically and chemically it would be expected that the thinning would be uniform over the whole surface. It not, it would be expected that the normal dissolution process would be a flaw-assisted process or a flaw-centered process. The importance of this heterogeneity has been well demonstrated in a series of elegant experiments reported from the University of Manchester Institute of Science and Technology (151,174).

When the process of film thinning is being scrutinized investigations dealing with the structure of the oxide film along with its physical properties become pertinent. Wood et al (174) have presented a strong case for the significant involvement of flaws in the oxide film. Observations with optical microscopy and electron microscopy demonstrate clearly that aluminum oxide films on aluminum, even of zone refined quality, 99.9999% pure, regardless of surface finish, contain "flaws". These have been classified as mechanical flaws and residual flaws. The term mechanical flaws encompasses a large number of defects, including scratches, and flaws produced by crystallographic assymmetry. The term residual flaws originates from segregated phases such as Cu-Al or Fe-Al compounds in the respective alloys. Flaws with a population density of 10^4 to $10^5/cm^2$ are reported for films on 99.99% Al and as high as $10^{10}/cm^2$ on Al-Cu alloys. There is general agreement that surface oxide films contain flaws. Perhaps, the theory may be argued with on a quantitative basis, i.e., whether or not there are as many flaws as reported, but certainly, not on a qualitative basis, because many studies have demonstrated the heterogeneity of metal surfaces, and it is well known that oxides grown on metals experience an epitaxial type reproduction of surface geometry. The direct linkage of flaws to pit initiation is also reasonable, particularly because such sites would be preferred sites for adsorption, and once adsorption occurs the development of an active center should be a logical next step. The active center is then the site for accelerated film thinning.

The work of Pryor et al (82,175) can be discussed under film thinning because at this stage the focus is on the aluminum oxide film. Pryor views the oxide film on aluminum, that is, the film produced by anodization in ammonium tartrate solution at a pH of 7, as well as the air formed film, as a thin, uniform film of constant thickness throughout the pH range of 0-10. The anodized films used in the work were about 260 Å thick. The reactions were discussed in terms of a defect solid state model. The oxide film was considered to be a face-centered γ - Al_2O_3 structure similar to that produced by high temperature oxidation. The poorly developed long range order in the crystal structure was attributed to the inclusion of a small number of Al^{+++} ions in oxygen positions in the FCC lattice. Based on that assumption the further assumption was made that the corrosion reaction must involve, presumably in a rate determining step, the diffusion of aluminum ions and electrons through the oxide film via cation vacancies and anion vacancies as well. The adsorption of anions at the oxide-electrolyte supposedly produces a high electrical field which draws the aluminum ions through the film. To support this view measurements were made of the defect structure, crystal structure, and thickness of γ - Al_2O_3 films (initially 260 Å thick by anodizing) during immersion in solutions of sodium chloride, chromate, and fluoride. These measurements included a c capacitance and dissipation factor determinations at variable frequencies, electron microscope and electron diffraction, as well as observations with ellipically polarized light. According to these measurements, immersion of aluminum coated with these anodized films in sodium chromate and sodium chloride solutions at a pH of 6 produced no change in crystal structure or film thickness, But, immersion in NaCl solution did produce substantial decreases in the specific resistance of the film with time when measured at frequencies below 100,000 Hz. These results of lowered specific resistance in chloride solution were interpreted, still following the solid state model, to be due to the introduction of n-type current carriers by exchange of chloride ions from solution with oxide ions. Thus, the ionic, but not the electronic resistance, of the film was lowered. In sodium fluoride solution, supposedly gross contamination of the oxide occurred by "complex aluminum oxyfluoride". The capacitance curves were then interpreted in terms of an increase in average dielectric constant.

These experimental results are a useful contribution to the field of localized corrosion but their interpretation by the Authors is inconsistent with other experimental results and current thinking in the field. The use of a solid state model with the assumption of a uniform γ - Al_2O_3 layer itself is inconsistent with scanning electron micrographs as well as other surface analytical measurements. The development of a high electric field by chloride ion adsorption when the adsorption is represented as an exchange reaction with hydroxides is unrealistic. This model does not recognize well-documented evidence, such as the existence of flaws in the film, the existence of a hydrated oxide rather than an anhydrous γ - Al_2O_3 film, the specific nature of the anion reactions, or the difficulty in reconciling the effect of a critical pitting potential on corrosion. The basic question which is not answered satisfactory is the method in which Al^{+++}

ions pass into solution during the pitting process. The Pryor mechanism apparently involves the critical step as the lattice diffusion of Al^{+++} ions. Davies (176) has critically reviewed literature investigations on conduction in Al_2O_3. He concluded that Al_2O_3 is an ionic conductor with activation energies as follows; for oxygen transport, for extrinsic conductivity, 53 k cal/mole, and for intrinsic conductivity, 136 k cal/mole; for aluminum transport, for extrinsic conductivity, 15.2 k cal/mole and for intrinsic conductivity, 67 k cal/mole. For the solid state model proposed, the values for the intrinsic conductivity which is the sum of the enthalpies of mobility and formation of defects would be applicable. Activation energies for pit propagation were determined by Stirrup, et al (166) by measuring the rate of pit propagation (anodic pitting current) at a fixed potential increment (20 mV) from Ep at a series of temperatures. The average value was about 2.5 k cal suggesting a rate limiting solution diffusion process. The activation energies for pit initiation as reported in Table IV vary from 5.0 to 26.0 k cal depending on the anion and the pH. It must be concluded that the solid state model would predict kinetic results about an order of magnitude lower than those actually observed.

A simpler explanation of the change in electrical properties of the anodically formed oxide film is the conversion of amorphous alumina to hydrous aluminum oxide (199). This explanation for the deterioration of electrical properties is supported by the results of Konno et al (198).

VI: DIRECT ATTACK OF EXPOSED METAL

Once the film is sufficiently thinned, the high degree of reactivity of metallic aluminum insures rapid attack and pit propagation. Because, the film is thinned locally the attack on the metal will also be concentrated, in the geometrical sense. A schematic cross-section of the pit taken from the paper of Hübner and Wranglén (178) is shown in Figure 3. It is evident that a number of reactions or physical processes are involved at any one time. But, it should be emphasized that this step, the direct attack of the exposed metal, differs in a basic manner from the pit initiation reaction. The initiation reaction is concerned with the interaction, chemically or physically, of the oxide film with the solution (the environment). The growth of the pit, the propagation of the pit, involves the interaction of aluminum metal directly with an environment that is changing as the reaction proceeds. Recognizing this different behavior then the futility of disclosing a single phenomenon to correlate the entire four step pitting process becomes evident.

Furthermore, it is now recognized that the direct attack on any metal surface is not a smooth, continuous reaction. Rather, it is an erratic process and shows up in potential cycling. This has been demonstrated by Hagyard, et al (200) who observed the fluctuation of potential of the aluminum electrodes and by Hladsky and Dawson (201) who recorded the "electrochemical noise" generated by steel electrodes during pitting and crevice corrosion.

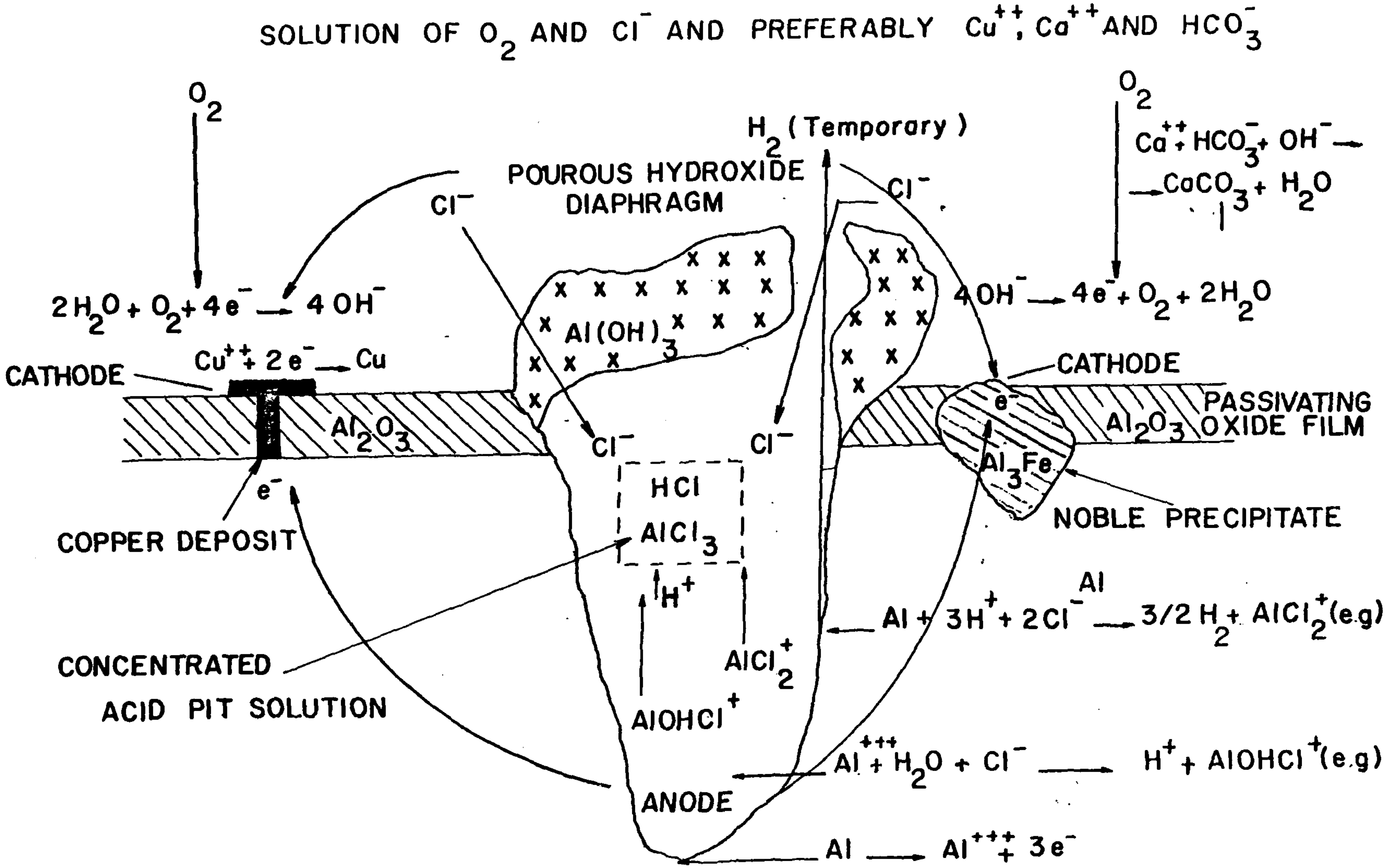

SOLUTION OF O2 AND Cl⁻ AND PREFERABLY Cu⁺⁺, Ca⁺⁺ AND HCO3⁻
O2
2H2O + O2 + 4e⁻ → 4OH⁻
Cu⁺⁺ + 2e⁻ → Cu
CATHODE
Al2O3
e⁻
COPPER DEPOSIT
CONCENTRATED ACID PIT SOLUTION
Cl⁻
POUROUS HYDROXIDE DIAPHRAGM
Al(OH)3
Cl⁻
HCl
AlCl3
H⁺
AlCl2⁺
AlOHCl⁺
ANODE
H2 (Temporary)
Cl⁻
Cl⁻
O2
Ca⁺⁺ + HCO3⁻ + OH⁻ → CaCO3 + H2O
4OH⁻ → 4e⁻ + O2 + 2H2O
CATHODE
e⁻
PASSIVATING Al2O3 OXIDE FILM
Al3Fe
NOBLE PRECIPITATE
Al + 3H⁺ + 2Cl⁻ →(Al) 3/2 H2 + AlCl2⁺ (e.g)
Al⁺⁺⁺ + H2O + Cl⁻ → H⁺ + AlOHCl⁺ (e.g)
Al → Al⁺⁺⁺ + 3e⁻

Figure 3. Multiple reactions going on in an aluminum pit (from Hubner and Wranglen, reference 178)

Nevertheless, there are certain features of this particular step upon which there is general agreement.

In practice pits are very seldom hemispherical or even of regular geometry, so equations developed on that premise must be considered very approximate indeed. However, with that understanding some empirical results might be reviewed. Dallek (179) made microscopic observations of the pit formed on AA 7075 in halide solutions, excluding fluoride solutions, and found that the pits were predominantly hemispherical. The rate of propagation expressed as current as a function of time took the form

$$i - i_p = a (t - t_i)^b \qquad [8]$$

where i = the dissolution current; i_p = the passive current; t = time; t_i = induction time; a = a constant dependent on the halide; and b = a constant dependent on the geometry of the pit. In Figure 1 the current-time curve for pitting initiation and propagation by Br^- ion in 1N H_2SO_4 is presented as a typical curve. A plot of log $(i - i_p)$ vs. log $(t - t_i)$ the slope of which is "b", is given in Figure 4. An equation similar to the above was obtained experimentally and derived theoretically by Engell and Stolica (162) for the pitting of iron by chloride solution. In their derivation they assumed that the pitting sites were hemispherical, that the dissolution current density was much greater than the passive dissolution current density and was proportional to the sum of the pit cross sectional areas, and that the rate of development of new pits was linearly dependent on time. According to the derivation, when the number of pits is constant with time, b is 2; when the number of pits

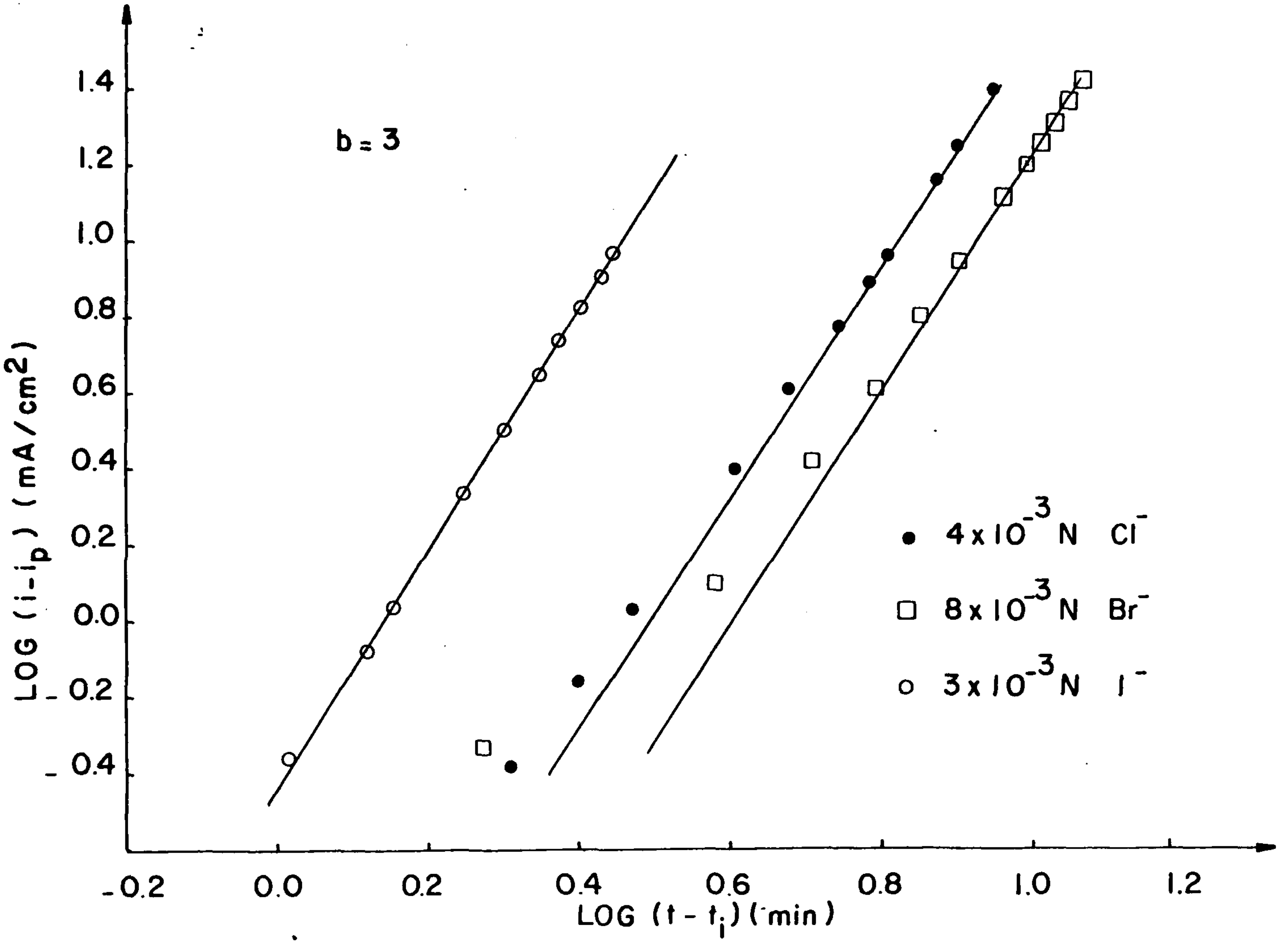


Fig. 4 Determination of "b" in pit growth equation. ●, Chloride solution, □, bromide solution, ○, iodide solution.

is proportional to time, b is 3. The data plotted for the aluminum alloy in Figure 4 apparently meet or approximate these specifications, as the data fit the cubic equation quite well. The data plotted in Figure 4 follow the equations

for 3×10^{-2}N I^- $\quad (i - i_p) = 0.073\ (t - t_i)^3$

for 4×10^{-3}N Cl^- $\quad (i - i_p) = 0.0051\ (t - t_i)^3$

for 8×10^{-3}N Br^- $\quad (i - i_p) = 0.00195\ (t - t_i)^3$

It is important to recognize that the behavior of aluminum alloys described here probably represents a special case insofar as the curves experimentally yield a b = 3 or exhibit cubic behavior. The literature on the kinetics of pitting has been extensively reviewed by Szlarska-Smialowska (180-1) and she has concluded that the Engell-Stolica treatment is oversimplified to apply in a general way to all cases of pitting. Rather, the pits should be placed in one of the three categories: (i) Case I: The pits are hemispherical and the radius of the pit approximates the pit depth; (ii) Case II: The pit is nonhemispherical, the radius is greater than the depth; (iii) Case III: The pit has a cylindrical shape with the radius less than the height of the cylinder. For this reason, experimentally, b values varying from 0.5 to greater than 5 have been obtained. Moreover, in the pitting of Ni in solutions containing various concentraions of $SO_4^{=}$ and Cl^- the b value changes with the ratio of the two ions. From the foregoing, it is concluded that a value of b = 3 conforms with hemispherical pits growing in cross section linearly with time with the number of pits also increasing linearly with time.

The morphology of the pit is affected by the potential as well as the specific anion involved in the pitting reaction.

There has been very little reported in the literature regarding the morphology of the pit as affected by the nature of the aggressive anion. Politycki and Fischer (100) described the different etching patterns formed on high purity aluminum by attack in HCl, HBr, HI, and HF. Cubic cavities were formed in HCl and HBr solutions, cubooctahedral cavities in HI, and no well-defined etch figures in HF solution. These patterns were explained in terms of steric relationships that derive from the direct contact between halide ions of a given radius with surface aluminum atoms separated by a given distance in the metallic lattice.

Lacombe et al (95-98) demonstrated the importance of crystallographic factors in the etching of high purity aluminum. The intercrystalline attack by HCl was attributed to actual discontinuities between grains furnishing a preferred site of attack. This etching was also observed in NaCl solutions on single crystals of aluminum. The "veining" was due to small blocks of units (within the single crystal) from which the crystal was build up possessing slightly different crystallographic orientation.

Heinrich et al (182) report on a microscopic study of pits in chloride-and nitrate-containing electrolytes. The actual geometry depends on the potential and the anion; cubic pits were observed in 0.1N NaCl; pyridmidal pits in a solution of 0.1N NaCl and 0.1N $NaNO_3$; and hemispherical pits in 0.1N $NaNO_3$. These studies offer convincing evidence for the crystallographic variance of pit propagation. Nguyen (171) observed, along with others, that the applied potential does influence the morphology of the pits that are formed on AA 1199 in chloride solution. At low potential $E_{appl.}$ (620 mV), the pits formed were hemispherical, while at high $E_{appl.}$ (1860 mV), the pit mouth was covered by a porous layer film with a small central orifice. It was also observed that gas bubbles out through this small orifice during the pitting process. This type of pitting behavior had also been reported for austenitic stainless steel at 860 mV (vs. NHE) by Makowski and Szklarska-Smialowska (183) as well as by Rosenfeld (184).

With respect to the morphology of pits grown on 99.99% Al produced by anodic polarization Kaesche (185) makes the general observation that pits grown at potentials near to the pitting potentials exhibit crystallographic etching whereas pits grown at potentials far from the pitting potential yield interiors which are smoothed from electropolishing.

Only with pure homogeneous alloys can regular geometrical pits be expected and even then as the pits are enlarged they assume an irregular geometry. This sub-surface behavior has been dramatically demonstrated in studies of the pitting of aluminum with the x-ray microscope (202) with which it is possible to follow the meandering of a pit just below the surface.

If the alloy contains segregated second phases preferential attack will occur at the sites. This usually leads to intergranular attack. During this last step in the pitting process the heterogeneity of the alloy assumes major importance. Up until this point the properties of the oxide film have been overshadowing. In this stage the electrochemical behavior of the heterogeneous metal surface becomes evident and coupled with the solution chemistry of the occluded cell becomes the dominant factor.

It has long been recognized that the heterogeneity of the alloy leads to accelerated attack. It is now known that heterogeneity can be enhanced during surface reaction and can be reflected in the nature of the corrosion product and perhaps in the mechanism of corrosion. Auger electron spectroscopy has revealed that Mg and Zn are heavily segregated at grain boundaries in an Al-Zn-Mg (AA 7075-T6) (203). It is postulated that the free Mg can be incorporated into the corrosion product film in the form of MgH or MgH_2 compounds, the hydrogen being produced by the reaction of aluminum with water. The formation of these compounds is then considered to prevent the formation and discharge of molecular hydrogen giving the atomic hydrogen time to diffuse into the meal and produce embrittlement. The evidence for the grain boundary segregation is substantial, the extrapolation to the subsequent hydrogen embrittlement mechanism and the part that it plays in the stress corrosion cracking of the alloy is speculative.

It has been shown in studies with photo-electron spectroscopy and secondary ion mass-spectrometry (204) that considerable surface enrichment of Li and Mg occurs during the thermal treatment of technically pure aluminum at temperature as low as 280°C. This surface enrichment is of the order of 4×10^3 for lithium and 1×10^3 for magnesium. This enrichment of these elements in the oxide layer is reflected in increased susceptibility of the aluminum foil to surface corrosion in the presence of humidity.

It has long been recognized that the composition of the solution within the corrosion pit differs substantially from that in the bulk solution. This also holds for the solution in a crevice and the advancing crack of a stress corrosion cracking specimen. Without knowledge of the pH of this solution and the chemical composition, including Al^{+++} ion concentration and anion concentration, it would not be possible to characterize the composition of the "occluded cell" sufficiently to formulate a reasonable mechanism for the pitting process. For this reason a considerable amount of effort has been expended to analyze the solution in a stress-corrosion crack, in pits, and crevices, both artificial and naturally occurring. Generally speaking, these analyses are quite close to each other.

The first attempt to analyze the solution at the crack tip in an aluminum alloy was made by Brown, et al (186). They developed a freezing technique to contain the solution at the tip of propagating crack in NaCl solution and found that the pH at the crack tip was acidic (pH - 3.5), and aluminum ions were present. Those findings were the first experimental confirmation of the prediction made by Edeleanu and Evans (187) that, after corrosion starts, the composition of the solution inside a pit or a (stress corrosion) crack should be different from that in the body of the solution. Referring to aluminum pitting, they concluded that due to imperfect mixing, the H^+ accumulating within the pit must be equivalent to the OH^- accumulating outside the pit and the latter is responsible for the observed continued slow rise in pH in the body of the solution.

Rosenfeld and Marshakov (188) constructed artificial crevices and measured corrosion currents that developed between otherwise equal electrodes, one in a crevice, and the other with free access of electrolyte (0.5N NaCl). A corrosion current of 160 $\mu A/cm^{-2}$ developed, with the electrode in the crevice functioning as the anode. The solution in the crevice immediately became acid and attained a pH of 3.2 to 3.4. They explained this value by the hydrolysis of the Al^{+++} ion to give $Al(OH)^{++}$. From the hydrolysis constant of 1.4×10^{-5}, they calculated a pH of 3.5. This now appears to be the correct interpretation of this pH.

Later, Sedriks, et al (189) attempted to simulate the environment existing inside the crack by using the turnings of aluminum alloy immersed in initially acid (pH 0, 1, and 2) solutions of NaCl. They used small solution-aluminum ratios to simulate the geometry of the crack. They found that the pH initially started to increase and then subsequently reached a steady value of approximately 3.5 which led them to propose that the attainment of a steady pH was determined by the solubility product of aluminum hydroxide and is directly related to the amount of free aluminum ions in solution. However, aluminum hydroxide is not the stable species at a pH of 3.5 (191).

Using microelectrodes having tip diameters of 1 to 5 micrometers, Davis (192) working with AA 7075-T651 in a solution 4.4% KCl in H_2O at a pH 5.8 to 6.2, observed that the pH in the vicinity of the crack tip was the most acidic and increased as the pH probe tip was moved toward the bulk solution. Also, the pH at the crack tip changed only slightly when the pH of the bulk solution was varied in the range of 2 to 10.

Unfortunately, most of the experimental work on the occluded cell has been done in chloride solution, and the results, e.g. an observed pH of 3.2, have been extrapolate to all electrolytic solutions. Recently (193) the analysis of the solutions obtained with the freeze-thaw technique of Brown from stress corrosion cracks in AA 7075 cracked in 1N NaCl, Na_2SO_4, $NaNO_3$, and $NaClO_4$ have become available. A summary of the pH's in the crack and the pre-crack zone (which resembles a crevice) are given in Table VI). The corresponding Al^{+++} ion analysis are given in Table VII. These results demonstrate that the behavior in chloride, and to some degree sulfate, differs appreciably from that in nitrate, perchlorate, and H_2O. The results in perchlorate are of special interest because perchlorate ion does not form

Table VI. Analysis of Stress Corrosion Crack Solutions - pH measurements. (from ref. 193)

Electrolyte	pH			
	Crack tip	Corrosion product region	Precrack region	Bulk Solution
1N NaCl	3.0-3.2	4.2 - 4.5	4.6 - 5.0	7.0 - 7.2
1N $NaClO_4$	6.1-6.3	6.6 - 6.9	6.9 - 7.2	7.0 - 7.2
1N $NaNO_3$	5.9-6.1	6.6 - 6.9	7.0 - 7.2	7.0 - 7.2
1N Na_2SO_4	6.1-6.3	2.8 - 3.0	4.0 - 4.3	7.0 - 7.2
H_2O	6.6-6.9	6.9 - 7.2	6.9 - 7.2	6.9 - 7.2

Table VII. Analysis of Stress Corrosion Crack Solutions - Aluminum Ion Concentration and Potential (from ref. 193)

Electrolyte	Concentration of Al^{+++} (molar)		Potential of Bulk Solution (vs SHE)	Plateau Crack Rate (10^{6} cm sec^{-1})
	Corrosion crack region	Precracked region		
1 N NaCl	0.025(10)*	0.36(5)	-0.588 V	1.43
1 N $NaClO_4$	0.008(9)	0.39(8)	-0.524 V	0.81
1 N $NaNO_3$	0.005(5)	0.18(5)	-0.111 V	0.48
1 N Na_2SO_4	0.005(5)	0.36(6)	-0.443 V	0.29
H_2O	-	-	-	0.61

*number of measurements that were averaged to get the reading reported metal-anion complexes. These results were unexpected. Following, what had been reported in the literature it had been assumed that at the anode, the tip of the crack, Al^{+++} would go into solution and a concentrated solution of the aluminum salt of the respective anion would be formed. The corrosion rates of AA 1199 and AA 7075 had been determined in 0.1N, 0.2N, and 0.5N solutions of $Al(NO_3)_3$, $AlBr_3$, $AlCl_3$, $Al_2(SO_4)_3$, $AlClO_4$, and AlI_3 (189). The corrosion rates varied with the salt but for all of these solutions the rates were very high. All of these salts are the neutralization product of the respective strong acid and the weak base, $Al(OH)^{++}$. These salts upon hydrolysis gave pH's for the 0.5M solutions of 1.10 to 3.49 with most about 2.5. Therefore, it was expected that the analyses of the solution in the stress corrosion crack for the four electrolytes would be approximately the same.

These latest findings lead to the conclusion that, insofar as, the solution in the advancing crack of a stress corrosion cracking specimen is concerned, and the artificial crevice produced in the pre-cracked specimen is concerned, the pH and the aluminum concentration are anion dependent. There was no evidence for very concentrated solutions of the aluminum salt and certainly no evidence for precipitated salt films as has been reported in the literature.

One complicating factor that has been observed in the examination of stress corrosion cracks and presumably will be observed in pits and crevices is the alteration of the chemical species as the reaction ensues (194).

It is known that nitrate is reduced by elemental aluminum in alkaline solution (195) which alkaline solution can be produced in the pit at the cathodic site

$$8Al^\circ + 3NO_3^- + 5OH^- + 18H_2O \rightarrow 8Al(OH)_4^- + 3NH_3 \qquad [9]$$

When a solution of $NaNO_3$ was brought in contact with aluminum powder, the formation of ammonia could be recognized after 16 hours. Upon shaking the suspension vigorously, the formation of NH_3 was quickly accelerated and within a few minutes, the heat generated by the reaction brought the whole solution to complete ebullition. Since no such formation of NH_3 was observed in the case of alumina, it was concluded that NH_3 was the product of the chemical reaction between NO_3^- and the underlying aluminum metal.

The cathodic reaction occurring within the pit, or on the pit shoulder, may be either the reduction of oxygen or the reduction of H^+ ions. Schikorr (196) in 1933 pointed out that the corrosion of aluminum takes place with the evolution of hydrogen when conditions favor the formation of $AlCl_3$ and NaOH at different sites which do not interact. Recently (197) it has been postulated that the production of hydrogen and the formation of blisters by the excessive hydrogen pressure is a precursor to pitting, that is, hydrogen evolution is involved in pit initiation rather than pit propogation.

VII. CONCLUSIONS

Localized corrosion, as evidenced by pits, crevices, intergranular attack, and stress corrosion cracking of high strength aluminum alloys is a multi-step process. It has been found to be more logical in the analysis and review of localized corrosion to recognize the multi-step character of the process, than it is to formulate a General Theory of Localized Corrosion and then to attempt to warp all experimental findings into this framework.

Such an approach is more practical and useful for the corrosion engineer who is interested in corrosion mitigation. A recognition of the role of adsorption and chemical reaction would direct the search for species that would be competitively adsorbed, in opposition to aggressive ions, and would react to form low energy compounds. The environment might be adjusted to balance film thinning with film repair. The chemical composition of the occluded cell could be altered to lower pit propagation rate. The potential could be brought low enough to prevent pitting and yet not so low as to generate alkali (amphoterism).

The elimination of any one of the four steps in the process would provide a profitable approach to the elimination of localized corrosion.

VIII REFERENCES

1. G.H. Bailey, Engineering 95, 374, 379 (1912)

2. E. Maass and W. Wiederholt 17, 115-21 (1921)

3. F. Mylius, Z. Metallkunde, 17, 148-54 (1925)

4. L.W. Haase, Z. Elektrochem. 32, 286-9 (1926)

5. N. Izgaruishev and V. Jordanskii, Korrosion u. Metallschutz 3, 54-8 (1927)

6. H. Winkelmann, Korrosion 2, 49-53 (1927)

7. J.M. Bryan, Dept. Sci. Ind. Research (Brit) Food Inv. Board 1936, 196-203

8. R.B. Mears and R.H. Brown, Ind. Eng. Chem. 29, 1087-91 (1937)

9. W. Stewart Patterson and J.H. Wilkinson, J. Soc. Chem. Ind 57, 445-6 (1938)

10. F.A. Champion, Trans. Faraday Soc. 41, 593-610, (1945)

11. A.B. McKee and R.H. Brown, Corrosion, 3, 613-31 (1947)

12. J. Meybeck and N. Iwanow, Bull. Inst. Textile France No. 36, 7-26 (1952)

13. W. Beck, F.G. Keihn and R.G. Gold, J. Electrochem. Soc. 101, 393-9 (1954)

14. V.H. Troutner, U.S. Atomic Energy Comm. HW - 50133, 53 pp (1957)

15. O. Sverepa, Werkst. u. Korros. 9, 533-6 (1958)

16. K.F. Lorking and J.E.O. Mayne, J. Appl. Chem. (London) 11, 170-80 (1961)

17. N. Merbaul, Dechema Monograph 45, 289-98 (1962)

18. J.D. Talati, Indian J. Technol. 1 (6), 254-5 (1963)

19. K.F. Lorking, Australasian Corrosion Eng. 7 (8) 25-30 (1963)

20. K.F. Lorking, Aust. Aeronaut. Res. Labl., Met. Rep., ART/MET-61 (1969)

21. H. Boehni, Schweiz. Arch. Angew Wiss. Tech. 36, 41-5 (1970)

22. A.M. McKissick, A.A. Adams, and R.T. Foley, J. Electrochem. Soc., 117, 1459-60 (1970)

23. F.D. Bogar and R.T. Foley, J. Electrochem. Soc. 119, 462-4 (1972)

24. P.L. Bonora, G.P. Ponzano, and V. Lorenzelli, Brit. Corros. J. 9, 112 (1974)

25. R. Seligman and P. Williams, J. Soc. Chem. Ind., 35, 88-93 (1916)

26. K. Kino, J. Chem. Soc. Chem. Ind. Japan, 40, 312 (1937)

27. M. Staub, Ann. Chim. 1 (12), 105-56 (1946)

28. M. Stern and H.H. Uhlig, J. Electrochem. Soc. 99, 381-8 (1952), 100, 543-52 (1953)

29. J.D. Minford, M.H. Brown, and R.H. Brown, J. Electrochem. Soc. 106, 185-91 (1959)

30. J.D. Talati and B.M. Patel, Indian J. Technol., 7, 62-3 (1969)

31. T.E. Kil'chevskaya, Zh. Prikl. Khim., 43, 1062-8 (1970)

32. J.D. Talati and B.M. Patel, Indian J. Technol. 8, 228-30 (1970)

33. L.R. van Dillen, C. Knaus, G.M. Kraay, and R. Riebl, Arch. Rubbercultuur, 12, 61-125 (1928)

34. J.M. Bryan, Dept. Sci. Ind. Research (Brit) Rept. Food Invest. Board. 1935, 170-80

35. J.M. Bryan, Dept. Sci. Ind. Research (Brit) Rept. Food Invest. Board, 1937, 201-7 (1938)

36. J.M. Bryan, J. Sci. Food Agr. 1. No. 3, 84-7 (1950)

37. R. Landau, Corrosion 8, 283-8 (1952)

38. W. Wiederholt, Metall. 7, 343-7 (1953)

39. T. Hagyard and J.R. Santhiopillai, J. Appl. Chem. (London), 9, 323-30 (1959)

40. M. Raupach, Australian J. Soil. Res. 1, 28-35, 36-45, 46-54, 55-62 (1963)

41. M. Katoh, Corros. Sci. 8 (6), 423-31 (1968)

42. R.T. Foley, J. Electrochem. Soc. 122, 1493 (1975)

43. V. Caglioti, Gazz. Chim. Ital. 66, 549-51 (1936)

44. W.M. Latimer and W.L. Jolly, J. Am. Chem. Soc. 75, 1548-50 (1953)

45. I.W. Köhler, Werskt. u Korros., 6, 478-56 (1955); 9, 20-5 (1958)

46. Y. Chapron, Commis. Energ. At. (Fr). Rapp. No. 3031, 103 pp (1966)

47. K.F. Lorking and J.E.O. Mayne, Brit. Corrosion J. 1 (5), 181-2 (1966)

48. M. Kotoh, J. Electrochem Soc. Japan (Overseas) 35 (3), 142-6 (1967)

49. K.H. Brown, B.E. Roetheli, and H.O. Forest, Ind. Eng. Chem. 23, 350-2 (1931)

50. Y. Kondo and S. Nomura, Denki Kagaku, 31, 54-61 (1963)

51. W.A. Bell and H.S. Campbell, Brit. Corrosion J. 1, 72-9 (1965)

52. K. Videm, Kjeller Rept., KR 88, 12 pp., (1966)

53. W. Vedder and D.A. Vermilyea, Trans. Faraday Soc. 65, 561-84 (1969)

54. O. Tegun, Keikinzoku, 18, 127-38 (1968)

55. K. Horibe, Keikinzoku, 18, 579-85 (1968)

56. K. Videm, Kjeller Report KR-149, Institute for Atommenergi (1974)

57. C.K. [illegible]nkler and H. Masters, Analyst. 49, 30-52 (1924)

58. L.H. Callender, Engineering, 120, 340-2 (1925)

59. H. Bohner Hauszeit V.A.W. Erft. A.G. Aluminium, 3, 347-8 (1931)

60. J.W. Smith, Light Metals 1, 124-5 (1938)

61. L. Reschke and H. Neunzig, Aluminium 23, 358-62 (1941)

62. J.F.J. Thomas, Can. J. Research 21B, 43-53 (1943)

63. G.T. Colegate, Metallurgia 39, 316-318 (1949)

64. R.B. Mears and R.H. Brown, J. Electrochem. Soc. 97, 75-82 (1950)

65. W. Machu, Ann. Univ. Ferrara, Ser. 5, Suppl. 4 (1), 153-76 (1966)

66. V.P. Kassyura and E.M. Zaretskii, Zashch. Metal. 4 (4) 376-80 (1968)

67. D.B. Boies and B.J. Northam, Mater. Prot. 7, 27-30 (1968)

68. D.M. Brasher, Centre Belge Etude Doc. Eaux 300, 523-31 (1968)

69. Z.A. Foroulis, Symp. Coupling Basic Appl. Corros. Res. Dialogue 1966, 24-37 (1969)

70. V. Kapali, S.V. Iyer, and N. Subramanyan, Brit. Corros. J. 4, 305-8 (1969)

71. T.L. Rama Char and D.K. Padma. Trans. Inst. Chem. Eng. 47, T 177-82 (1969)

72. J.M. Abdel-Kader and A.M.S. El Din Corros. Sci. 10, 551-9 (1970)

73. M.N. Desai, S.M. Desai, M.H. Gandhi, and C.B. Shah, Anti-Corros. Methods Mater. 18, 9-13 (1971)

74. N. Subramanyan and V. Kapali, Corros. Sci. 11, 55-7 (1971)

75. M.N. Desai, Werkst. Korros. 23, 475 (1972)

76. S.C. Makwana, N.K. Patel and J.C. Vora, J. Indian Chem. Soc. 50, 664 (1973)

77. B.W. Samuels, K. Sotoudeh and R.T. Foley, Corrosion, 37, 92-97 (1981)

78. G.H. Bailey, J. Soc. Chem. Ind., 39, 118-20 (1920)

79. W.J. Müller, Korrosion u. Metallschutz, 12, 132-8 (1936)

80. S. Yamaguchi, Bull. Chem. Soc. Japan, 18, 53-91 (1943) (German)

81. J.M. Bryan, J. Soc. Chem. Ind (London) 69, 169-73 (1950)

82. M.J. Pryor, Z. Elektrochemie 62, 782-94 (1958)

83. S. Tajima, M. Soda, T. Mori, and N. Baba, Electrochemica Acta 1, 205-16 (1959)

84. V.H. Troutner, Corrosion 15, 9t - 12t (1959)

85. P.M. Aziz and H.P. Godard, Corrosion, 15, 642t (1959)

86. K.F. Lorking, J. Appl. Chem. (London) 10, 449-56 (1960)

87. E.C. Hoxie and M.A. Post, U.S. Atomic Energy Comm. TID-1528, 13 pp. (1962)

88. A.J. Pollard, Rept. NRL Progr. 1964 (P.B. No. 181, 563), 1-2

89. S. Mori and J.E. Draley, J. Electrochem. Soc. 114 (4), 352-3 (1967), 353-4 (1967)

90. G.D. Bengough and H. Sutton, Engineering 122, 274-77 (1926)

91. I.S. Kerr, Proc. Phys. Soc. (London) 69B, 1055-56 (1956)

92. I.G. Murgulescu, O. Radovici, and S. Ciolac, Corrosion Sci., 4, 353-61 (1964)

93. E. Scarano and M. Forina, Ann. Chim. 56, 580-97,598-609 (1966)

94. R. Winand, Metallurgia, 12, 122 (1972)

95. P. Lacombe and L. Beaujard, Compt. Rend. 219, 66-8 (1944)

96. P. Lacombe and N. Yannaquis, Compt. Rend. 224, 921-2 (1947)

97. P. Lacombe and N. Yannaquis, Rev. met. 45, 68-77 (1948)

98. P. Lacombe and L. Beaujard, Rev. met. 45, 317-22 (1948)

99. E.C.W. Perryman, J. Metals 5, Trans. 911-17 (1953)

100. A. Polityzki and H. Fischer, Z. Elektrochem. 57, 393-9 (1953)

101. I. Sato, Denki Kagaku, 24, 506-11 (1956)

102. T.H. Oren, J. Research Natl. Bur. Standards 58, 157-67 (1957)

103. V.H. Troutner, Corrosion 15, 7t - 8t (1959)

104. G. Wyon, Compt. rend. 247, 458-61 (1958)

105. H.P. Godard and W.E. Cooke, Corrosion, 16, 181t - 187t (1960)

106. J.J. McMullen and M.J. Pryor, Intern. Congr. Metallic Corrosion, 1st. London, Engl. 1961, 52-9 (1962)

107. A.C. Fraker and A.W. Ruff, Corrosion, 27, 151-6 (1971)

108. M.J. Pryor, Corros. Sci. 11, 463 (1971)

109. B.A. Wilson, Corros. Sci. 11, 527 (1971)

110. R. Alwitt and L.C. Archibald,Corr. Sci., 13, 687-8 (1973)

111. L. Lepina and Z. Osis, Latvijas PSR Zinatnu Akad. Vestis (1950) No. 6 (Whole No. 35) 35-46; (1952) No. 8 (Whole No. 61) 107-13

112. L. Liepina, A. Vaivade, Z. Osis, and A. Striprais, Latvijas PSR Zinatnu Acad. Vestis, (1954), No. 3 (Whole No. 80) 107-13

113. L. Liepina and A. Vaivade, Latvijas PSR - Zinatnu Akad. Vestis, Kim. Ser. (1963) (3), 297-304; (1963) (6), 683-8; (1964), 441-7; (1964) (5), 527-33.

114. L. Liepina and V. Kadek, Corrosion Sci. 6 (3-4), 177-181, (1966)

115. L. Liepina, Latvijas PSR Zinatnu Akad. Vestis (1967) (3), 55-64

116. E. Maass and W. Wiederholt, Korrosion u. Metallschutz 5, 265-70 (1929)

117. G.V. Akimov and A.I. Glukhova, Compt. Rend. Acad. Sci. URSS 49, 194-7 (1945)

118. H. Makram, Compt. rend. 244, 3153-4 (1957)

119. E. Deltombe and M. Pourbaix, Corrosion 14, 496t - 500t (1958)

120. T. Morzumi, Hokkaido Daigaku Koga Kubu Kenkyu Hokoku 1967 (42) 123-31 (1967)

121. J. Calvet, Compt. rend. 188, 1111-4 (1929)

122. W. Krönig, Korrosion u. Metallschutz, 7, 104-8 (1931)

123. W.J. Müller and E. Low, Aluminium, 18, 478-86, 541-4 (1936)

124. E. Kuhnrich, Aluminium, 20, 83-5 (1938)

125. J.R. Galvele and S. DeMicheli, Corros. Sci. 10, 795-807 (1970)

126. P.R. Shibad and J. Balachandra, J. Electrochem. Soc. India, 20, 58-60 (1971)

127. E. D. Verink, Jr. and D.B. Bird Materials Protection 7, 28-32 (1967)

128. G. Akimov, First Comm. New Intern. Assoc. Testing Materials (Zurick) D, 127-40 (1930)

129. L. Cavallaro and G.P. Bolognesi, Atti. accad. sci. Ferrara 29, 121-32 (1952)

130. D.E. Davies, J. Appl. Chem. (London) 9, 651-9 (1959)

131. S.L. Chrisholm, Mater. Protect. 3, 54-64 (1964)

132. S. Tajima, T. Mori, and M. Komiya Boshoku Gijutsu, 14, (3), 109-117 (1965)

133. T.J. Lennox, M.H. Peterson, J.A. Smith, and R.E. Groover, Mater. Performance 13, 31 (1974)

134. H. Lonmel, Korrosion, 25, 29-34 (1974)

135. J.V. Petrocelli and A. Phillips, Trans. Electrochem. Soc. 85, 20 pp preprint (1944)

136. G. Masing and G. Maldehnke-Hohmann, Z. Metallkunde 42, 19-23 (1951)

137. R. Ergang, G. Masing and M. Möhling, Z. Elektrochem. 55, 160-5 (1951); 56, 8-16 (1952)

138. K.M. Carlsen, J. Electrochem. Soc. 104, 147-54 (1957)

139. E.M. Khairy and M.K. Hussein, Corrosion 13, 793t-798t (1957)

140. F.H. Haynie and S.J. Ketcham, Corrosion 19, 403t - 407t (1965)

141. K.F. Lorking, Australia Commonwealth, Dept. Supply, Aeron. Res. Lab. Rept. MET, 54, 13pp (1964)

142. E.G. Bohlmann and F.A. Posey, U.S. At. Energy Comm. ORNL - P - 1430, 29, pp. 1965

143. H. Boehni and H.H. Uhlig, J. Electrochem. Soc. 116, 906-10 (1969)

144. G.A. Dibari and H.J. Read, Corrosion 27, 489-93 (1971)

145. H. Kaesche, Proc. Int. Congr. Metal Corros., 4th 1969, 15, (1972)

146. R. Graner and E. Wiedmer, Werkst. Korros. 24, 128-30 (1973)

147. A. Broli, H. Holtan, and K.L. Prestrud, Corrosion 30, 427 (1974)

148. A. Berzins, R.T. Lowson, and K.J. Mirams, Aust. J. Chem. 30, 1891 (1977)

149. L. Kawano, N. Baba, and S. Tajima Denki Kagaku, 40, 29-32, 632-6 (1972)

150. N. Subramanyan and K. Ramakrishnarak, Trans. Soc. Advan. Electrochem. Sci. Technol. 7, 100 (1972)

151. G.C. Wood, J.A. Richardson, M.F. Abd. Rabbo, L.B. Mapa, and W.H. Sutton in "Passivity of Metals" pp 973-988 ed. by R.P. Frankenthal and J. Kruger, The Electrochemical Society, Princeton, N.J. (1978)

152. J. Augustynski, ibid. pp. 989-1002.

153. J.A. Richardson and G.C. Wood, Corros. Sci. 10, 313 (1970)

154. J.A. Richardson and G.C. Wood, J. Electrochem. Soc. 120, 193 (1973)

155. G.A. Parks, Chem. Rev. 65, 177 (1965)

156. L. Campanella, F. Croce, and P. Mazzoni, Oberflaeche - Surf. 19, 224 (1978)

157. L. Campanella, J. Electroanal. Chem. 28, 228-232 (1970)

158. K. Nisancioglu and H. Holtan, Corros. Sci. 18, 835 (1978)

159. A. Broli and H. Holtan, Corros. Sci. 13, 237-246 (1973)

160. A. Broli, H. Holtan, and H. Sigurdsson, Werkst. u. Korrosion, 26, 629-633 (1975)

161. N. Nilsen and E. Bardal, Corros. Sci. 17, 635-646 (1977)

162. H.J. Engell and N.D. Stolica, Z. Physik. Chem., N.F. 20, 113 (1959)

163. S. Dallek and R.T. Foley, J. Electrochem. Soc. 123, 1775 (1976)

164. K.J. Laidler, "Chemical Kinetics" 2nd ed. p. 286, McGraw-Hill, New York (1965)

165. Z.A. Foroulis and M.J. Thubrikar, J. Electrochem. Soc. 122, 1296 (1975)

166. B.N. Stirrup, N.A. Hampson, and I.S. Midgley, J. Applied Electrochemistry 5, 229-235 (1975)

167. R.C. Turner and G.J. Ross, Can. J. Chem. 48, 723, (1970)

168. G. Sussek, M. Kesten, and H.G. Feller, Metall. 33, 1031 (1979); 33, 1276 (1979)

169. G. Johannson, Acta Chem. Scand. 16, 403 (1962)

170. R.T. Foley and T.H. Nguyen, J. Electrochem. Soc. 129, 464-467 (1982)

171. T.H. Nguyen and R.T. Foley, J. Electrochem. Soc. 126, 1855-1860 (1979)

172. R.W. Smith, "The State of Al(III) in Aqueous Solution and Adsorption of Hydrolysis Products on α-Al_2O_3" Dissertation, Stanford University (June 1969)

173. E.B. Sandell, "Colorimetric Determination of Traces of Metals" InterScience Publishers, Inc., New York, (1950)

174. G.C. Wood, W.H. Sutton, J.A. Richardson, T.N.K. Riley and A.G. Malherbe, in "Localized Corrosion", pp. 526-546 ed. by R.W. Staehle, B.F. Brown, J. Kruger, and A. Agrawal NACE, Houston, Texas (1974)

175. M.J. Pryor, ibid pp. 2-11

176. M.O. Davies, NASA Tech. Note, NASA TN D-2765

177. T.H. Nguyen and R.T. Foley, J. Electrochem Soc. 127, 2563-2566 (1980)

178. W. Hubler and G. Wranglen, Proc. 4th Scand. Corros. Congr. (1964), p. 60

179. S. Dallek and R.T. Foley, J. Electrochem. Soc. 125, 731-733 (1978)

180. Z. Szklarska-Smialowska, Corrosion 27, 223 (1971)

181. Z. Szklarska-Smialowska, Werkst Korros 22, 780 (1971)

182. H. Heinrich, N. Kanani, and H.G. Feller, Aluminium 54, 198-202 (1978)

183. J. Makowski and Z. Szklarska-Smialowska, Corros. Sci., 15, 493 (1975)

184. I.L. Rosenfeld and I.S. Danilov, in "Proceedings of 3rd International Congress on Metallic Corrosion" Vol. 1 p. 139, Moscow (1969)

185. H. Kaesche, in "Passivity of Metals" pp. 935-959 ed. R.P. Frankenthal and J. Kruger, The Electrochemical Society, Princeton, New Jersey (1978)

186. B.F. Brown, C.T. Fujii and E.P. Dahlberg, J. Electrochem. Soc. 116, 218 (1969)

187. C. Edeleanu and U.R. Evans, Trans. Faraday Soc. 47, 1121-1135 (1951)

188. I.L. Rosenfeld and I.K. Marshakov, Corrosion, 20, 115t - 125t (1964)

189. K. Sotoudeh, T.H. Nguyen, R.T. Foley and B.F. Brown, Corrosion 37, 358-62 (1981)

190. A.J. Sedriks, J.A.S. Green, and D.L. Novak, Corrosion, 27, 198-202 (1971)

191. C.F. Baes, Jr. and R.E. Mesmer, "The Hydrolysis of Cations, John Wiley and Sons, New York (1976)

192. J.A. Davis, in "Localized Corrosion" ed. by R.W. Staehle, B.F. Brown, J. Kruger, and A. Agrawal, pg 168, NACE, Houston, Texas (1974)

193. Anh H. Le and R.T. Foley, Corrosion, submitted for publication.

194. T.H. Nguyen, R.T. Foley, and B.F. Brown, J. Electrochem. Soc. 129, 780-781 (1982)

195. P.C.L. Thorne and E.R. Roberts, "Fritz Ephraim Inorganic Chemistry, 5th ed. p. 620, Gurney and Jackson, London (1949)

196. G. Schikorr, Mitt. deut. Materialprufungsanstatt Sonderheft 22, 22-5 (1933)

197. C.B. Bargeron and R.B. Givens, Corrosion 36, 618-625 (1980)

198. H.B. Konno, S. Kobayashi, H. Takahashi, and M. Nagayama, Corrosion Science 22, 913-923 (1982)

199. W.J. Bernard and J.J. Randall, Jr. J. Electrochem. Soc. 108, 822 (1961)

200. T. Hagyard, W.B. Earl, and M.J. Prior, Trans. Faraday Soc. 57, 2288-2298 (1961)

201. K. Hladsky and J.L. Dawson, Corrosion Science, 21, 317-322 (1981)

202. R.T. Foley and S.P. Newberry, J. Phys. Chem. 62, 1184 (1958)

203. R.K. Viswanadham, T.S. Sun, and J.A.S. Green, Metallurgical Transactions 11A, 85-89 (1980)

204. M. Textor and R. Grauer, Corrosion Science 23, 41-53 (1983)

END

DATE
FILMED

9 - 83

DTIC